# PATENT ABSTRACTS OF JAPAN

(11)Publication number:

2001-150559

(43) Date of publication of application: 05.06.2001

(51)Int.CI.

B29C 70/30 // B29K 35:00 B29K105:12

(21)Application number : 11-336561

(71)Applicant : SEKISUI CHEM CO LTD

OKAYAMA SEKISUI KOGYO KK

(22)Date of filing:

26.11.1999

(72)Inventor: NISHIYAMA MASAKI

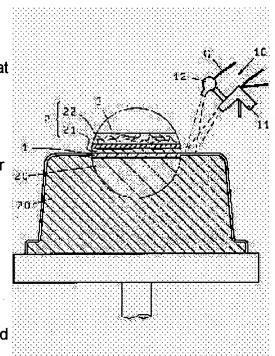
KAWACHI FUJIO

## (54) FIBER-REINFORCED RESIN MOLDING AND METHOD FOR MANUFACTURING THIS RESIN **MOLDING**

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a fiber-reinforced resin molding with a presentable appearance showing such advantages that a defoaming operation is easy and the productivity can be enhanced and further, the presence of air bubbles between a fiber-reinforced layer and a corrugated layer is almost not allowed without the generation of warpage due to heat shrinkage or curing shrinkage after molding and also the generation of a glass mark as well as a method for manufacturing this fiber-reinforced resin molding.

SOLUTION: This fiber-reinforced resin molding is structured of an intermediate layer 2 formed of a dicyclopentadiene unsaturated polyester resin containing an inorganic filler between a corrugated layer 1 and a fiber-reinforced resin layer 3. In addition, the fiberreinforced resin layer 3 is formed of the dicyclopentadiene unsaturated polyester resin.



### **LEGAL STATUS**

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

\* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the fiber strengthening resin mold goods used for an organ bath, a washing place, etc., and its manufacture approach.

[0002]

[Description of the Prior Art] As for the fiber strengthening resin mold goods used for an organ bath etc., watertightness, thermal resistance, etc. are required. Conventionally, this kind of fiber strengthening resin mold goods had the common thing in which the gel coat layer was formed on the front face of the fiber reinforcement resin layer which mixed reinforcement fiber, such as a glass fiber and a carbon fiber, in thermosetting resin, such as an unsaturated polyester resin, as die length of about 25-50mm.

[0003] In such mold goods, if air bubbles with a diameter of 1mm or more exist between a fiber reinforcement resin layer or a fiber reinforcement resin layer, and a gel coat, a gel coat layer will be destroyed by giving an elevated temperature and low temperature repeatedly like an organ bath. an exterior -- if a gel coat layer is destroyed, dirt will adhere to the destroyed part -- while becoming unsightly, it also becomes the cause of leakage of water. For this reason, the fiber strengthening resin mold goods used for an organ bath etc. must remove air bubbles from between a fiber reinforcement resin layer or a fiber reinforcement resin layer, and gel coat layers. It is it easy to generate an atmospheric-air bubble in the corner of mold goods that especially the die length of reinforcement fiber is also 25-50mm, and a degassing activity cannot be done easily. For this reason, it is easy to generate a degassing defect and variation arises in quality.

[0004] By the way, in case the layered product which has a fiber reinforcement resin layer by the spray up method is formed from the former, as an approach for removing air bubbles, reinforcement fiber sprays a die in an unsaturated polyester resin under reduced pressure, a lamination (fiber reinforcement resin layer) is formed for example, in the Japanese Patent Publication No. 59-No. 35765 official report, and, subsequently to this lamination, the method of collapsing air bubbles by forming an airtight surface layer and exposing under atmospheric pressure is indicated. Moreover, an unsaturated polyester resin is sprayed with the reinforcement fiber of glass roving at a die, a fiber reinforcement resin layer is formed, and, subsequently to this fiber reinforcement resin layer, the approach of forming an airtight surface layer and pressurizing is indicated by the Provisional-Publication-No. 60-No. 124237 official report. [0005] Also in which the above-mentioned approach, since it is necessary to form an airtight surface layer and reinforcement fiber does not contain in this surface layer, the reinforcement of mold goods falls. Moreover, by the approach indicated by the Japanese Patent Publication No. 59-No. 35765 official report, a vacuum chamber is required and a facility will become large-scale. By the approach indicated by the Provisional-Publication-No. 60-No. 124237 official report, by the time mold goods harden completely, it must be recuperated within a pressure tank in these mold goods, and the time amount in which these mold goods occupy a pressure tank becomes long, productivity worsens, and it is not economical, then, as an approach of reducing mixing of air bubbles between a lamination (fiber reinforcement resin layer) or a lamination, and a gel coat layer, without using a vacuum chamber and a pressure tank Spray a die in comparatively short reinforcement fiber and thermosetting resin, and the 1st lamination (staple fiber reinforcement resin layer) is formed. Then, after spraying this 1st lamination in comparatively long reinforcement fiber and thermosetting resin and forming the 2nd lamination (continuous glass fiber reinforcement resin layer), the method of stiffening the 1st and 2nd laminations is proposed (for example, refer to Japanese Patent Publication No. 7-No. 22972 official report).

[0006

[Problem(s) to be Solved by the Invention] However, although the degassing activity was easy and productivity improved by the manufacture approach of the fiber strengthening resin mold goods indicated by the above-mentioned Japanese Patent Publication No. 7-No. 22972 official report The 1st lamination (staple fiber reinforcement resin layer) containing comparatively short reinforcement fiber (staple fiber) has many pitches. Contraction of fiber strengthening

resin mold goods took place by hardening contraction by contraction of an unsaturated polyester resin, while deformation of mold goods, such as hardening contraction after shaping, arises, the glass eye of a glass fiber loomed, the glass mark has arisen, and exterior inferiority carries out.

[0007] Moreover, the 1st lamination (staple fiber reinforcement resin layer) containing a staple fiber may generate small air bubbles in a layer by the permutation with the air of the front face of a glass fiber, when resin sinks into a glass fiber, although generating of air bubbles decreased, and it is \*\*. In the degassing activity with a roller, these small air bubbles are difficult to remove, and had a problem used as the defect on the quality of mold goods.

[0008] It is in offering fiber strengthening resin mold goods excellent in the appearance which this invention solves the above-mentioned problem, air bubbles cannot intervene easily between a fiber-reinforcement resin layer and a gel-coat layer as if a degassing activity is easy for the place make into the purpose and improvement in productivity can be aim at, camber does not produce in a heat shrink, hardening contraction, etc. after shaping, and a glass mark does not generate, and its manufacture approach.

[0009]

[Means for Solving the Problem] In order to attain such a purpose, the middle class who consists of a dicyclopentadiene system unsaturated polyester resin containing an inorganic bulking agent is prepared between a gel coat layer and a fiber reinforcement resin layer, and the fiber strengthening resin mold goods (it is hereafter described as "the fiber strengthening resin mold goods of claim 1") concerning invention according to claim 1 are characterized by the resin of a fiber reinforcement resin layer consisting of a dicyclopentadiene system unsaturated polyester resin [0010] The fiber strengthening resin mold goods (it is hereafter described as "the fiber strengthening resin mold goods of claim 2") concerning invention according to claim 2 shall consist of the 1st middle class whom the middle class turns into from the dicyclopentadiene system unsaturated polyester resin containing an inorganic bulking agent, and the 2nd middle class who contained 3-20mm reinforcement fiber in fiber length at least in the fiber strengthening resin mold goods of claim 1.

[0011] The manufacture approach (it is hereafter described as "the manufacture approach of the fiber strengthening resin mold goods of claim 3") of the fiber strengthening resin mold goods concerning invention according to claim 3 The process which the gel coat resin which is the approach of manufacturing fiber strengthening resin mold goods by the spray-up-moulding method, and consists of thermosetting resin on a die is sprayed [ process ], and forms and stiffens a gel coat layer, The process which sprays this gel coat layer in the dicyclopentadiene system unsaturated polyester resin containing an inorganic bulking agent, and forms an interlayer, It consists of a process which sprays this middle class in reinforcement fiber and a dicyclopentadiene system unsaturated polyester resin, and forms a fiber reinforcement resin layer before this middle class hardens, and a process which stiffens said middle class and a fiber reinforcement resin layer.

[0012] The manufacture approach (it is hereafter described as "the manufacture approach of the fiber strengthening resin mold goods of claim 4") of the fiber strengthening resin mold goods concerning invention according to claim 4 In the process which forms the interlayer in the manufacture approach of the fiber strengthening resin mold goods of claim 3 In the process which forms the middle class, on the hardened gel coat layer, spray the dicyclopentadiene system unsaturated polyester resin containing an inorganic bulking agent, and the 1st middle class is formed. This 1st middle class is sprayed in at least 3-20mm reinforcement fiber and a dicyclopentadiene system unsaturated polyester resin, and the 2nd middle class is formed.

[0013] In this invention, especially as thermosetting resin used for a gel coat layer, it is not limited, for example, an unsaturated polyester resin and vinyl ester resin are mentioned. Moreover, although a maleic anhydride and a cyclopentadiene may be made to add by the reaction, and methylene tetrahydro phthalic anhydride may be compounded, for example as a cyclopentadiene system unsaturated polyester resin used for the middle class and a fiber reinforcement resin layer by this invention and this may be used as one component of polyester resin, what added the direct unsaturated polyester resin at the time of manufacture, and carried out system partial saturation of the dicyclopentadiene which dimerizes to resin manufacture and coincidence may be used. In addition, an abovementioned unsaturated polyester resin and an above-mentioned dicyclopentadiene system unsaturated polyester resin usually contain vinyl monomers for bridge formation, such as styrene, and are used.

[0014] In the fiber strengthening resin mold goods of claims 1-2, the HANDORE rising method or a spray up method is adopted as a fabricating method which forms a fiber reinforcement resin layer. In the case of the HANDORE rising method, an interlayer is formed on a gel coat layer, and about this interlayer, although a laminating is carried out by the \*\*\*\*\* method, arranging a fiberglass mat, glass fabrics, or woven glass roving, and infiltrating resin on an interlayer since full hardening is carried out, in the case of a spray up method, it becomes semi-hardening or the approach an interlayer and a fiber reinforcement resin layer spray and carry out the laminating of the dicyclopentadiene system unsaturated polyester resin using a spray gun.

[0015] In this invention, it is desirable for powder, such as a calcium carbonate, a glass bead, and glass balun, to be mentioned, and to be blended in the range of the 60 - 100 weight section generally to the dicyclopentadiene system

unsaturated-polyester-resin 100 weight section as an inorganic bulking agent contained in the dicyclopentadiene system unsaturated polyester resin used in the middle class. Under in 60 weight sections, viscosity falls, it starts at the time of shaping and there is fault of producing the liquid lappet of resin in a field, and since viscosity will cause and spray a spray gun highly and proper \*\* will worsen if the 100 weight sections are exceeded, poor shaping is produced.

[0016] It is what was used together with the hardening accelerator as a curing catalyst if needed to the curing agent or such a curing agent which consists of organic peroxide, and the curing agent disassembled below about 40 degrees C is used. Here, as organic peroxide, methyl ethyl ketone peroxide, cyclohexanon peroxide, methyl acetoacetate peroxide, a cumene hydroperoxide, etc. are used. Moreover, as a hardening accelerator, naphthenic-acid cobalt, dimethylaniline, and an acetylacetone are mainly used. As for such a curing agent, it is desirable to be blended in the range of 0.5 - 3 weight section generally to the above-mentioned unsaturated-polyester-resin, vinyl-ester-resin, or dicyclopentadiene system unsaturated-polyester-resin 100 weight section.

[0017] the die length of the reinforcement fiber contained in the 2nd interlayer -- the range of 3-20mm -- it considers as the range of 6-15mm preferably. Moreover, as for the die length of content \*\*\*\* reinforcement fiber, it is desirable in a fiber reinforcement resin layer that it is the range of 20-30mm for a long time than the die length of the reinforcement fiber contained at the 2nd interlayer.

[0018] As thickness of the layered product of mold goods, it is the range whose thickness of a gel coat layer is 0.2-1.0mm, and it is desirable that the 1st interlayer's thickness is 0.4-0.8mm and the range whose thickness of the 2nd interlayer is 0.4-1.5mm. Moreover, as for the thickness of a fiber reinforcement resin layer, it is desirable that it is the range of 0.5-1.5mm.

[0019]

[Embodiment of the Invention] Below, the example and the example of a comparison of this invention are shown. <u>Drawing 1</u> is the schematic diagram of the laminating configuration explaining the fiber strengthening resin mold goods and its manufacture approach of this invention.

[0020] (Example 1) In the unsaturated polyester resin (styrene 40% is contained as a cross linking agent monomer) which uses isophthalic acid as the main raw material, the organ bath draw spike as a die 20 was sprayed with the spray gun 11 of the spray-up machine 10 as a gel coat resin, mixing a curing agent, and the gel coat layer 1 with a thickness of 0.3mm was formed and stiffened.

[0021] Next, the dicyclopentadiene system unsaturated-polyester-resin (Dainippon Ink & Chemicals [, Inc. ] make: FS-980) 100 weight section, The polyester resin of the shape of putty which comes to blend the calcium-carbonate 80 weight section as an inorganic bulking agent Mixing the curing agent (methyl ethyl ketone peroxide) 1.5 weight section, spray the gel coat layer 1 with a spray gun 10, and the 1st interlayer 21 with a thickness of 0.5mm is formed. Furthermore, the dicyclopentadiene system unsaturated-polyester-resin (Dainippon Ink & Chemicals [, Inc. ] make: FS-980) 100 weight section, The polyester resin of the shape of putty which comes to blend the calcium-carbonate 80 weight section as an inorganic bulking agent While spraying on the 1st interlayer 21 with a spray gun 10, mixing the curing agent (methyl ethyl ketone peroxide) 1.5 weight section The fiber spraying machine 12 cuts the glass roping G as reinforcement fiber, the with a die length of 12mm inside fiber 15 weight section is sprayed, and the 2nd interlayer 22 with a thickness of 0.5mm is formed.

[0022] Then, on the 2nd middle class 22, while spraying the dicyclopentadiene system unsaturated-polyester-resin (NIPPON SHOKUBAI Industries make: SD-2100) 100 weight section with a spray gun 11, mixing a curing agent, the fiber spraying machine 12 cuts the glass roping G as reinforcement fiber, the continuous glass fiber 15 weight section 43 weight section with a die length of 25mm is sprayed, and the reinforcement fiber layer 3 with a thickness of 0.8mm is formed. While having not hardened an interlayer 2 and the fiber reinforcement resin layer 3, a roller is made to \*\*\*\* by the predetermined pressure on the fiber reinforcement resin layer 3. Degassing of the air bubbles generated in the 2nd interlayer 22 and the fiber reinforcement resin layer 3 by this is carried out. Since reinforcement fiber is not mixing this degassing activity in the 1st interlayer 21, the degassing activity with a roller is easy. Finally, after the law evasion activity, the interlayer 2 and the fiber reinforcement resin layer 3 were stiffened, and the fiber strengthening resin mold goods of an organ bath configuration were obtained.

[0023] since these fiber strengthening resin mold goods have little hardening contraction of a dicyclopentadiene system unsaturated polyester resin -- the surface sink on the front face of shaping, and a glass eye -- coming up (glass mark) -- etc. -- there is no surface discontinuity, and since an interlayer 2 is resin of the shape of putty containing a bulking agent, there are no air bubbles in the gel coat layer 1 side, and he does not make the gel coat layer 1 destroy [0024] (Example 2) The 2nd interlayer 22 was not formed in formation of the interlayer 2 of an example 1. In this case, an interlayer's 2 thickness was performed like the example 1 as 0.8mm except it, and the fiber strengthening resin mold goods of an organ bath configuration were obtained. consequently, the example 1 -- the same -- the surface sink on the front face of shaping, and a glass eye -- coming up (glass mark) -- etc. -- there were not surface discontinuity and air bubbles.

[0025] (Example 3) The calcium-carbonate 80 weight section as an inorganic bulking agent was not blended with the

dicyclopentadiene system unsaturated polyester resin which forms the 2nd middle class 22 in formation of the middle class 2 of an example 1. Except it, it carried out like the example 1 and the fiber strengthening resin mold goods of an organ bath configuration were obtained. Consequently, although the surface sink on the front face of shaping was carrying out small generating rather than the example 1, the glass eye came up by existence of an interlayer's 2 putty-like resin (glass mark), and there were no air bubbles.

[0026] (Example 1 of a comparison) In formation of the fiber reinforcement resin layer 3 of an example 1, it replaced with the dicyclopentadiene system unsaturated-polyester-resin 100 weight section, and considered as the unsaturated-polyester-resin 100 weight section which uses isophthalic acid as the main raw material. Except it, it carried out like the example 1 and the fiber strengthening resin mold goods of an organ bath configuration were obtained. Consequently, although the glass eye came up by existence of an interlayer's 2 putty-like resin (glass mark) and there were no air bubbles, the surface sink on the front face of shaping has occurred.

[0027] (Example 2 of a comparison) The 1st interlayer 21 was not formed in formation of the interlayer 2 of an example 1. Except it, it carried out like the example 1 and the fiber strengthening resin mold goods of an organ bath configuration were obtained. Consequently, although there was no surface sink on the front face of shaping as well as an example 1, the glass eye came up by the interlayer 2 containing a glass fiber (inside fiber of 12mm die length) (glass mark), and small air bubbles are generated. These air bubbles are hard to be removed in a degassing activity. [0028] (Example 3 of a comparison) It replaced with the dicyclopentadiene system unsaturated-polyester-resin 100 weight section used for the 1st middle class 21 and 2nd middle class 22 in formation of the middle class 2 of an example 1, and the unsaturated-polyester-resin 100 weight section which uses isophthalic acid as the main raw material was used. Except it, it carried out like the example 1 and the fiber strengthening resin mold goods of an organ bath configuration were obtained. Consequently, although the glass eye came up by existence of an interlayer's 2 putty-like resin (glass mark) and there were no air bubbles, the surface sink on the front face of shaping had occurred. [0029] (Example 4 of a comparison) In the example 2, it replaced with the dicyclopentaliene system unsaturatedpolyester-resin 100 weight section used for the middle class 2 and the fiber reinforcement resin layer 3, and the unsaturated-polyester-resin 100 weight section which uses isophthalic acid as the main raw material was used. Furthermore, instead of [ which does not blend the calcium carbonate as an inorganic bulking agent with an interlayer's 2 unsaturated polyester resin was sprayed with the fiber spraying machine 12 in the glass fiber (staple fiber of 3mm die length) 15 weight section, and the interlayer 2 was formed in it. Except it, it carried out like the example 2 and the fiber strengthening resin mold goods of an organ bath configuration were obtained. Consequently, as compared with the case of mixing of the inside fiber of the interlayer 2 in the example 2 of a comparison, although the magnitude of air bubbles became small, air bubbles were still generated, the glass eye of an interlayer's 2 staple fiber and the continuous glass fiber of the fiber reinforcement resin layer 3 came up (glass mark), and the surface sink on the front face of shaping had occurred.

[0030]

[Effect of the Invention] As above-mentioned, air bubbles cannot intervene easily between a fiber reinforcement resin layer and a gel coat layer, and the fiber strengthening resin mold goods of claims 1-2 turn into mold goods excellent in the appearance which camber does not produce in a heat shrink, hardening contraction, etc. after shaping, and a glass mark does not generate. Moreover, a degassing activity becomes easy and the manufacture approach of the fiber strengthening resin mold goods of claims 3-4 can aim at improvement in productivity while being able to obtain mold goods excellent in the appearance which air bubbles cannot intervene easily between a fiber reinforcement resin layer and a gel coat layer, camber does not produce in a heat shrink, hardening contraction, etc. after shaping, and a glass mark does not generate.

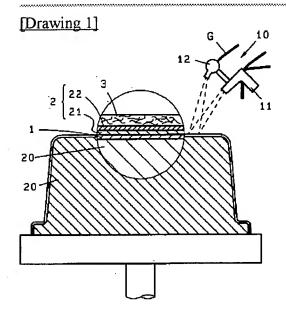
[Translation done.]

\* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **DRAWINGS**



[Translation done.]